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A perturbation theory approach to the calculation of density of states function in heavily doped germanium crystal

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An account of the calculation of the density of states function in degenerate germanium crystal applying non-degenerate, time-independent first and second order perturbation theories is presented here. The results suggest larger band tailing with increase in the impurity concentrations and the possibility of representing the density of states function in the extremely heavily-doped condition by a linear function on energy. The narrowing of energy gap of semiconductors with increase in the lattice temperature can be easily understood on the basis of this treatment.

1. Introduction

The invention of tunnel diode warranted a thorough investigation of the properties of degenerate materials. Since then such materials have also found applications in semiconductor laser diodes, thermoelectric generators, semiconductor catalysts, etc. A number of theories by Baltensperger (1953), Kane (1963), Bonch Bruyevich (1966) etc. have appeared since then to explain numerous features of heavily doped semiconductors. Here, however, we will be concerned with the method of Parmenter (1955) originally meant for disordered alloys.

The corrections to the energy of the system as a result of the first and second order, non-degenerate, time-independent perturbation theory (Schiff 1949) are

$$E_{1i} = H_{1i}' = \int \psi_{0i}^* H' \psi_{0i} dV \tag{1}$$

$$E_{2i} = \sum_{(j \neq i)} |H'_{ij}|^2 (E_{0i} - E_{0j})^{-1}. \tag{2}$$

We will be applying these equations in our derivations discussed below.

2. First order Density of States Calculation

When a crystal becomes heavily doped with impurity atoms, its true crystalline nature is disturbed in the sense that the crystal potential no longer remains perfectly periodic. However, impurity atoms may reasonably be assumed to occupy substituational lattice sites and their potentials may be regarded to perturb the potential energy of electrons in an otherwise perfect crystal.

First of all we apply first order time-independent perturbation theory in order to calculate the density of states function in a degenerate material. The screened Coulomb potential energy due to an impurity atom may be written as,

$$V_s'(r) = -\frac{A_s}{r}\exp(-ar) \qquad \ldots (3)$$

where,

$$A_s = \frac{q^2}{4\pi K\epsilon_0}\ ;\ \frac{1}{a} = (\pi K\epsilon_0)^{\frac{1}{2}}(\pi/3)^{1/6}\sqrt{a_0 N_i^{-1/3}} \qquad \ldots (3a)$$

and

$$a_0 = \frac{\hbar^2}{mq^2};\quad \text{First Bohr radius.}$$

Now if there are N_i impurity atoms per N atoms of the crystal, the system may be reduced to one in which there is one impurity atom per (N/N_i) atoms of the crystal. In such a case the unperturbed normalized electronic wave functions should be written as,

$$\psi_{0i} = \frac{1}{\sqrt{(N/N_i)\Omega}}\exp(-ik.r), \qquad \ldots (4)$$

where Ω is the volume of the unit cell of the crystal. The first order correction to the energy of the electrons is then,

$$E_{1i} = H_{ii} = \int \psi_{0i}^* H' \psi_{0i} dV. \qquad \ldots (5)$$

Substituting the values of ψ_{0i} in eq. (5), we get

$$E_{1i} = \frac{N_i}{N\Omega}\int_\infty \exp\,(i(k_i - k_j).r) H' dV$$

$$= \frac{N_i}{N\Omega}\int_\infty V_s'(r) dV, \qquad \ldots (6)$$

as H' = correction to the original Hamiltonian $= V_s'(r)$.

Therefore,
$$E_{1i} = -\frac{N_i}{N\Omega}\int_\infty \frac{A_s}{r}\exp(-ar) r^2 dr \sin\theta\, d\theta\, d\phi$$

i.e.,
$$= -\frac{N_i}{N\Omega}\int_0^\infty A_s\, r\exp(-ar)dr \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi = -\frac{4\pi N_i A_s}{N\Omega a^2}. \qquad \ldots (7)$$

As a result of this first order correction in energy, the electron energy modifies to

$$E = E_0 + E_{1i} = \frac{\hbar^2 k^2}{2m^*} - \frac{4\pi N_i A_s}{N\Omega a^2}. \qquad \ldots (8)$$

In order to determine an expression for the density of states function, we assume, n to be the total number of quantum states per unit volume of electrons having wave vector $\leqslant k$. As the volume of a Brillouin zone representing (N/N_t) quantum states is $(2\pi)^3/\Omega$ the volume of the k-space representing one quantum state would therefore be $(2\pi)^3/(N/N_t)\Omega$. Thus,

$$n = 2.\frac{\frac{4}{3}\pi k^3}{(2\pi)^3 \Big/ \left(\frac{N}{N_t}\right)\Omega} \times \frac{1}{\left(\frac{N}{N_t}\right)\Omega} = \frac{k^3}{3\pi^2}. \qquad \ldots (9)$$

The above expression has been multiplied by 2 to include the effect of electron spin.

The density of states function $\rho_1(E)$, according to its denifiition, should then be written as,

$$\rho_1(E) = \frac{dn}{dE} = \frac{dn}{dk} \cdot \frac{dk}{dE} . \qquad \ldots (10)$$

From eq. (8) we have $\frac{dE}{dk} = \frac{\hbar^2 k^2}{m^*}$ and from eq. (9), we have

$$\rho_1(E) = \frac{m^* k}{\pi^2 \hbar^2} = \frac{\sqrt{2m^{*3/2}}}{\pi^2 \hbar^3} \left\{ E + \frac{4\pi N_t A_s}{a^2 N \Omega} \right\}^{\frac{1}{2}} \qquad \ldots (11)$$

on substituting the value of k from eq. (8).

If N_t is put equal to zero in the above expression, we find that $\rho_1(E)$ reduces to the expression of the unperturbed density of states function $\rho_0(E)$ appropriate for an infinite potential well. The effect of the first order perturbation is thus seen to produce a shift in the origin of the unperturbed density of states function by an amount $\frac{4\pi N_t A_s}{a^2 N \Omega}$ into the band gap of the material.

3. Second Order Density of States Calculation

The correction to the electron energy as a result of the second order perturbation is written as (eq. 2).

$$E_{2i} = \sum_{(j \neq i)} |H'_{ij}|^2 (E_{0i} - E_{0j})^{-1}$$

where

$$H'_{ij} = \int_{\infty} \psi_{0i}^* H' \psi_{0j} \, dV$$

$$= \frac{N_t}{N\Omega} \int_{\infty} \exp(i(k_j - k_t).r) H' dV$$

$$= \frac{N_t}{N\Omega} \int_{\infty} \exp(ik.r) H' dV. \qquad \ldots (12)$$

H' = correction to the Hamiltonian = $V(r) = -A_s \frac{\exp(-ar)}{r}$,

Theresore, $$H'_{ij} = \frac{N_i}{N\Omega} \int_{\infty} \exp(ik.r) V(r) dV$$

or $$|H'_{ij}|^2 = \left(\frac{N_i}{N\Omega}\right)^2 |V(k)|^2$$

where, $$V(k) = \int_{\infty} \exp(ik.r) V(r) dV$$

But as $$E_{0i} = \frac{\hbar^2}{2m^*} k_i^2; \quad \text{and} \quad E_{0j} = \frac{\hbar^2}{2m^*} k_j^2$$

we have $$(E_{0i} - E_{0j}) = \frac{\hbar^2}{2m^*}(k_i^2 - k_j^2)$$

$$= \frac{\hbar^2}{2m^*}(-k)(2k_i + k),$$

where $$-k = k_i - k_j.$$

Therefore, second order correction to energy is

$$E_2 = -\left(\frac{N_i}{N\Omega}\right)^2 \frac{2m^*}{\hbar^2} \int \frac{|V(k)|^2 (2k_i k + k^2)^{-1}}{(2\pi)^3 \left|\left(\frac{N\Omega}{N_i}\right)\right.} dV_k, \qquad \ldots (13)$$

as the elementary volume of phase space is the volume occupied by a single quantum state $= (2\pi)^3 \Big/ \left(\frac{N\Omega}{N_i}\right)$

Thus,

$$E_2 = -\frac{N_i}{N\Omega} \frac{1}{(2\pi)^3} \frac{2m^*}{\hbar^2} \int_{\infty} |V(\sigma)|^2 (\sigma^2 + 2k_i\sigma)^{-1} dV_\sigma$$

$$= -\frac{N_i}{N\Omega} \frac{1}{(2\pi)^2} \frac{2m^*}{\hbar^2} \int_{\infty} |V(\sigma)|^2 \sigma^2 d\sigma I, \qquad \ldots (14)$$

where, $$I = \int_0^{\pi} \frac{\sin\theta \, d\theta}{2k_i\sigma \cos\theta + \sigma^2}, \qquad \ldots (15)$$

On evaluation $$I = -\frac{1}{2k_i\sigma} \ln \frac{\sigma - 2k_i}{\sigma + 2k_i}. \qquad \ldots (16)$$

Substituting eq. (16) in eq. (14), we get,

$$E_2 = \frac{N_i}{8\pi^2 N\Omega}\frac{m^*}{\hbar^2 k_i}\int_{-\infty}^{\infty} F(\sigma)d\sigma, \qquad \ldots (17)$$

where

$$F(\sigma) = |V(\sigma)|^2 \ln\frac{\sigma-2k_i}{\sigma+2k_i}\sigma \qquad \ldots (18)$$

and

$$V(\sigma) = \int_{\infty} \exp(i\sigma.r)V(r)dV$$

$$= \int_{\infty} \exp(i\sigma r\cos\theta)\frac{A_s}{r}\exp(-ar)r^2 dr\sin\theta\, d\theta\, d\phi$$

$$= A_s\int_0^a r\exp(-ar)dr\int_0^{\pi}\exp(i\sigma\, r\cos\theta)\sin\theta\, d\theta\int_0^{2\pi} d\phi. \qquad \ldots (19)$$

On evaluation of the above integral, we get,

$$V(\sigma) = 4\pi A_s(\sigma^2+a^2)^{-1}. \qquad \ldots (20)$$

Substituting eq. (20) in eq. (18), we get,

$$F(\sigma) = \frac{(4\pi A_s)^2}{(a^2+\sigma^2)^2}\,\sigma\ln\frac{\sigma-2k_i}{\sigma+2k_i} \qquad \ldots (21)$$

Substituting eq. (21) in eq. (17), we get,

$$E_2 = \frac{N_i}{8\pi^2 N\Omega k_i}\frac{m^*}{\hbar^2}\int_{-\infty}^{+\infty} F(\sigma)d\sigma.$$

Thus from the theorem of residues, we have,

$$E_2 = \frac{N_i}{8\pi^2 N\Omega k_i}\frac{m^*}{\hbar^2}2\pi_i\, R[F_s(ia)]$$

$$= -\frac{4\pi A_s^2 N_i}{a\Omega N}\frac{m^*}{\hbar^*}(a^2+4k^2)^{-1}. \qquad \ldots (22)$$

Now the total energy as a result of the second order perturbation becomes (taking E_1 = correction in energy due to first order perturbation = 0),

$$E = \frac{\hbar^2k^2}{2m^*} - \frac{4\pi A_s^2 N_i}{a\Omega N}\frac{m^*}{\hbar^2}(a^2+4k^2)^{-1}$$

i.e.,

$$4k^4+k^2\left(a^2-\frac{8m^*E}{\hbar^2}\right)-\frac{2m^*Ea^2}{\hbar^2}-\frac{8\pi m^{*2}A_s^2N_i}{\hbar^4N\Omega a}=0. \qquad \ldots (23)$$

As this is a quadratic equation in k^2, we get,

$$k^2 = \left(\frac{m^*E}{\hbar^2} - \frac{a^2}{8}\right) + \sqrt{\left(\frac{m^*E}{\hbar^2} + \frac{a^2}{8}\right)^2 + \frac{2\pi m^{*2} A_s^2 N_t}{\hbar^4 N \Omega a}}. \quad \ldots (24)$$

To obtain an expression for the density of states function we need calculate dk/dE which from eq. (24) works out to be,

$$\frac{dk}{dE} = \frac{m^*}{2k\hbar^2} + \frac{1}{2k}\left\{\left(\frac{m^*E}{\hbar^2} + \frac{a^2}{8}\right)^2 + \frac{2\pi m^{*2} A_s^2 N_t}{\hbar^4 N \Omega a}\right\}^{-1/2}\left(\frac{m^*E}{\hbar^2} + \frac{a^2}{8}\right)\frac{m^*}{\hbar^2}. \quad \ldots (25)$$

As we already know that $\frac{dn}{dk} = \frac{k^2}{\pi^2}$, we have,

$$\rho_2(E) = \frac{dn}{dE} = \frac{m^*E}{2\pi^2\hbar^2}\left[1 + \left(\frac{m^*E}{\hbar^2} + \frac{a^2}{8}\right)\left\{\left(\frac{m^*E}{\hbar^2} - \frac{a^2}{8}\right)^2 + \frac{2\pi m^{*2} A_s^2 N_t}{\hbar^4 N \Omega a}\right\}^{-\frac{1}{2}}\right.$$

$$\left. \times \left\{\left(\frac{m^*E}{\hbar^2} - \frac{a^2}{8}\right) + \sqrt{\left(\frac{m^*E}{\hbar^2} + \frac{a^2}{8}\right)^2 + \frac{2\pi m^{*2} A_s^2 N_t}{\hbar^4 N \Omega a}}\right\}^{\frac{1}{2}}\right].$$

4. Discussions

It has already been mentioned while calculating $\rho_2(E)$ that we have taken the correction in energy due to the first order perturbation as zero. Figure 1 shows the dependence of $\rho_2(E)$ as a function of energy for different impurity concentrations. We have taken $k = 16$, $\epsilon_0 = 8.854 \times 10^{-12}\ F/m$ and $m^* = 0.19$ m

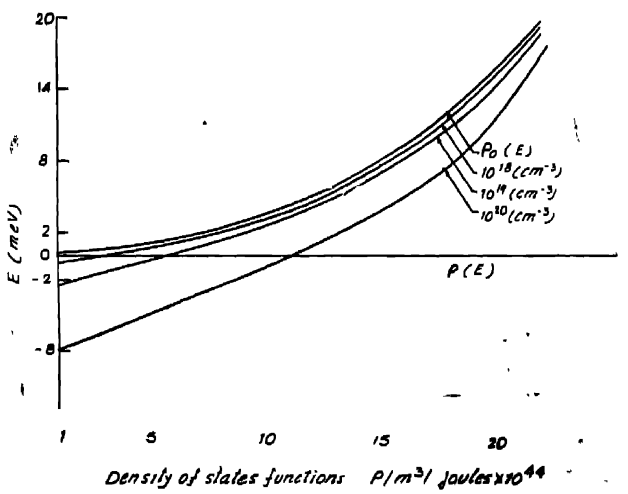

Fig. 1. Density of states function versus energy for different impurity concentration for germanium.

in our calculation. The entire second order density of states curves have, however, been shifted below by an amount equal to the first order energy correction to find out the net effect of perturbation. The curves very clearly illustrate that the density of states function tails into the band gap region with increase in the impurity concentration.

We note that the first order density of states curve retains its parabolic dependence on energy, while in the second order case we note that the curve deviates from its parabolic dependence and leans towards a linear nature. The exact nature of the density of states function in degenerate materials is, however, extremely complex. In the extreme case of heavy doping, when the material tends to become amorphous, the dependence of $\rho_2(E)$ on energy may, however, be taken as linear as an useful approximation. Such an approximation has been used by the authors to calculate the percentage of ionization in degenerate *n*-germanium. Such a calculation is required to estimate the fall in efficiency of thermoelectric generators derived on the assumption of complete ionization of carriers.

This perturbation theory calculation also explains the reason for narrowing of band gap of semiconductors with increase in the temperature of the crystal. Lattice vibrations may be regarded as perturbing the crystal potential and the density of states calculation in this case can also be carried out on similar lines as presented in this paper, to show that the energy gap of germanium crystal decreases with increase in temperature.

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Baltensperger W. 1953 *Phil. Mag.* **44**, 1355.
Kane E. O. 1963 *Phys. Rev.* **131**, 79.
Bonch-Bruyevich V. L. 1966 *The Electronic Theory of Heavily Doped Semi-conductors.* American Elsevier Pub. Co. Inc., New York.
Parmenter R. H. 1955 *Phys. Rev.* **97**, 587.
Schiff L. I. 1949 *Quantum Mechanics* McGraw-Hill Book Co., New York.
Roy D. K. & George P. J. 1975 *Solid State Electronics* **18**, 757.